

New Electrocatalysts for Fuel Cells

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Objectives

- Conduct research on the kinetics and mechanism of electrode reactions in low temperature fuel cells.
- Develop new electrocatalysts using a materials-by-design approach.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Electrode Performance

Approach

- Study the kinetics of fuel cell electrode reactions on well-characterized model electrodes and high surface area fuel cell electrocatalysts using modern electroanalytical methods.
- Study the mechanisms of the reactions using state-of-the art in-situ spectroscopies.
- Use ultrahigh vacuum (UHV) methods of surface preparation and surface analyses to form tailored surfaces.
- Synthesize nanoclusters to have the tailored surface.
- Characterize the microstructure of the nanoclusters by high-resolution electron microscopy.
- Transfer technology to catalyst developers/vendors.

Accomplishments

- Proof-of-principle experiments demonstrated that a Au-Pd alloy with <50 wt. % Pd can replace Pt as the hydrogen electrode catalyst without any loss in performance.
- Proof-of-principle experiments demonstrated that "Pt skin" structures with a non-precious metal core can be stable under proton exchange membrane fuel cell (PEMFC) air cathode operating conditions.

Future Directions

Cathode side:

- Create "skin" nanostructures of Pt on non-noble substrates and determine activity and stability as a novel low-Pt air cathode electrocatalyst. Select the most promising substrate for synthesis as high surface area catalyst.
- Develop and optimize a new class of non-Pt model catalysts. Synthesize and test new non-Pt high surface area catalysts at fuel cell conditions.

Anode side:

- Synthesize and characterize Pd-Au bimetallic nanoparticles and conduct preliminary testing as anodes in PEMFC hydrogen-air cells.
- Determine CO-tolerance of tailored electrodes consisting of thin films (1-10 monolayers) of Pd on the close-packed single crystal surfaces of Ta, Re, and W.

Introduction

It is known from the theory of surface segregation in bimetallic alloys that in certain systems, preferential surface enrichment in one element is so strong that it leads to a "skin" structure, i.e. the outermost layer is a "skin" of one element. Theoretically, for nanoparticles, such a segregating alloy system could form particles having a "grape" microstructure, a skin of one element over a core of the other. In principle, one could use this thermodynamic property to replace the "buried" atoms in Pt nanoparticles with a non-precious metal, e.g. Fe or Co, resulting in 100% Pt dispersion (all Pt atoms are surface atoms) without the need to create extremely small particles, e.g. <2 nm. For example, if a standard pure Pt catalyst consists of particles having on average a dispersion of 20%, replacement of the buried atoms in those particles with a base metal would enable the Pt loading to be reduced by a factor of 5, all other factors being the same. This is the basic strategy we are currently pursuing to reduce Pt loading in PEMFC cathodes.

Approach

Pt₃Ni and Pt₃Co are classical examples of alloys of Pt having a skin surface structure, a pure Pt skin. In this case, enrichment occurs by interchange of Pt and Co atoms between the first two atomic layers, the subsequent layers having the bulk composition (75% Pt). The thermodynamic driving force in this case is for the larger atom to be at the surface, since in face-centered cubic metals the surface is generally relaxed outward and the second layer contracted. The Pt₃Ni and Pt₃Co systems do not represent cases of the extreme segregation we need for replacing buried Pt atoms, but they do serve as a useful test case for the concept of a skin structure, and there appears to be a beneficial electronic effect for the Pt skin. Importantly, the Pt skin structure in Pt₃Co(Ni) was stable when used as an oxygen reduction electrode

under PEMFC conditions. The current approach is to extend the concept to Pt-refractory metal alloys, such as Pt-Re, Pt-W, or Pt-Ta. In these systems, the segregation is more extreme, driven by both the strain energy (Re and W are smaller atoms than Pt) and the surface tension; hence, the skin structure can be achieved with a lower bulk Pt concentration, replacing more buried Pt atoms with a non-Pt atom.

Results — Model Cathode Catalysts

Pt₃Re solid electrodes were prepared using conventional metallurgy and pre-treated in a surface analytical UHV chamber equipped with various instruments for surface preparation and analysis. As with Pt₃Co(Ni), for each alloy, either a pure Pt skin or a 75 at. % Pt surface could be prepared and tested as an oxygen reduction catalyst. The resulting activity for oxygen reduction as a function of composition is shown in Figure 1. The Pt skin structure on all three alloys is more active than the pure Pt reference surface, suggesting there is an

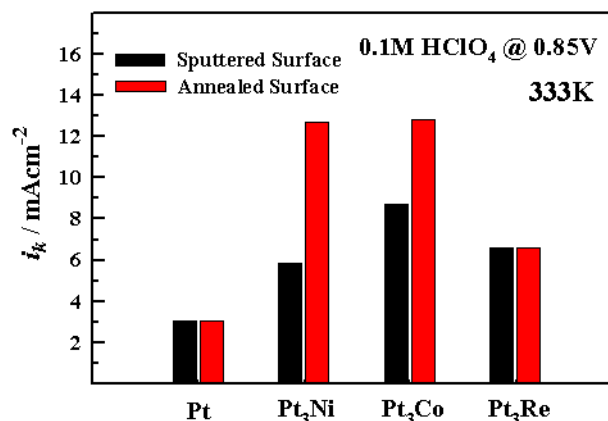


Figure 1. Steady-state current densities (per unit geometric area) at 0.85 V (vs. reversible hydrogen electrode—1 bar H₂, 333 K) for six different alloy electrodes vs. pure Pt: Pt skin on Pt₃Ni, Pt₃Co, and Pt₃Re (the annealed surfaces); and the 75% Pt surfaces on Pt₃Ni and Pt₃Co (the sputtered surfaces)

electronic effect that is generally beneficial for oxygen reduction kinetics. Importantly, the results represented in Figure 1 were obtained under the extreme conditions of use as an oxygen reduction electrode, e.g. continuous cycling between 0.1 – 1.0 V under 1 bar O_2 in acid electrolyte at 60°C produced no change in the cyclic voltammetry curves for the surfaces.

Epitaxial thin films of Pd on Pt(111) and Re(0001) single crystals were deposited either in UHV by a vapor deposition method or in-situ by purely electrochemical methods. The morphology was studied by a combination of ex-situ UHV surface analytical tools (low-energy electron diffraction, low-energy ion scattering—LEIS) and in-situ soft x-ray spectroscopy and Fourier transform infrared spectroscopy. Photoelectron spectroscopy (PES) results depicted in Figure 2a show that in the surface electronic density of states of the valence band, the position of the d-band center relative to the Fermi level is slightly lower for the pseudomorphic monolayer of Pd on Pt(111) than on bare Pt(111). The monolayer thickness was determined by LEIS (Figure 2b). Interestingly, such a small change in the surface electronic structure has a dramatic effect on the kinetics of the oxygen reduction reaction (ORR). In 0.1 M KOH, the general form of current vs. Θ_{Pd} relationship for the ORR has a volcano shape (Figure 2c), with the maximum catalytic activity exhibited by a surface modified with 1 monolayer (ML) of Pd. When the Pd deposit exceeds 1 ML, the catalytic activity is decreased linearly, with the Pd multilayer less active than unmodified Pt(111). This is strikingly similar to the “volcano relation” we reported here last year for the hydrogen oxidation reaction (HOR) on the same surfaces. For either the ORR or the HOR, there is no clear explanation for the volcano relation. On the side where $\Theta_{Pd} > 1$, the higher activity of the Pd monolayer versus the multilayer cannot be attributed to the effect of strain on the reactivity of metal surfaces proposed by Norskov and co-workers (Phys. Rev. Lett. 81(1998) 2819), since the strain is too small (+0.65% increase in the interatomic spacing). On the side where $\Theta_{Pd} < 1$, the increase in activity from the addition of an intrinsically less active metal is surprising and unexplained.

However, for the Pd film deposited on Re(0001), we were able to find a clear and compelling

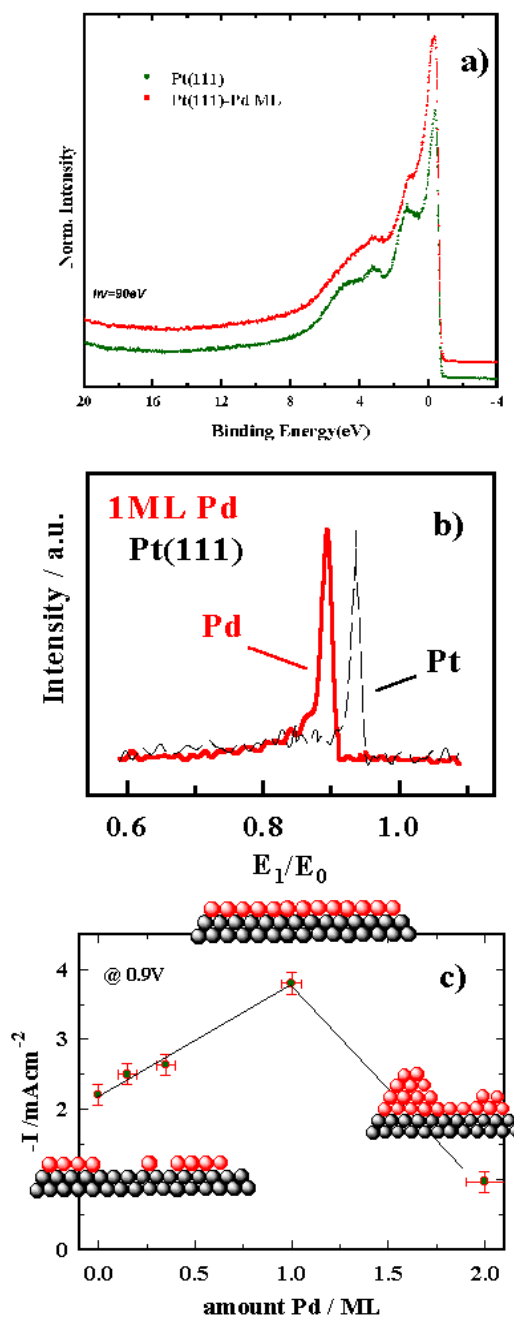


Figure 2. (a.) High-resolution UV ($h\nu = 90$ eV) photoelectron spectra in the valence band region for a Pd monolayer film on Pt(111) and the clean Pt(111) surface; (b.) LEIS spectra for the same surfaces showing the Pd layer is one atomic layer thick; (c.) Kinetics of ORR as a function of Pd coverage of Pt(111)

correlation between the electronic interaction of the Pd overlayer with the Re substrate and the resultant catalytic properties. The strong electronic interaction causes a significant narrowing of the d-band for the surface metal atoms (Figure 3a difference curve) with two relatively sharp peaks strikingly similar to the d-band of Ag(111). The d-band center, as defined by Norskov, is located ca. 1 eV below that of a Pd multilayer and/or that of the Pd deposited on Pt(111).

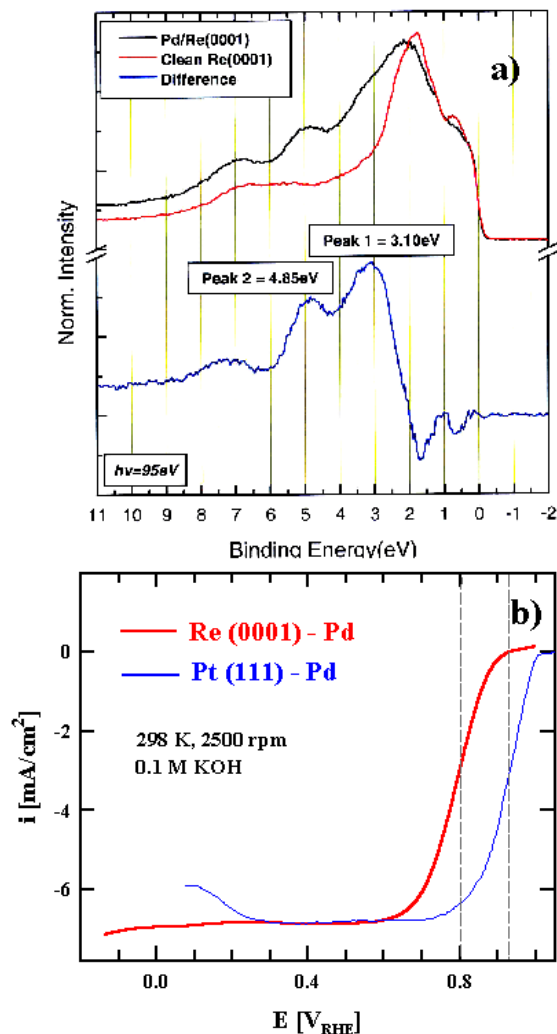


Figure 3. (a.) High-resolution UV ($h\nu = 90$ eV) photoelectron spectra in the valence band region for a Pd monolayer film on Re(0001) surface and the clean Re(0001) surface; (b.) Comparison of the polarization curves for ORR on the two different Pd monolayer films showing the dramatic effect of the electronic interaction with the substrate on the electrocatalytic properties of the Pd film

First principles density functional theory calculations by Norskov and co-workers for Pd/Re(0001) (Phys. Rev. B 60 (1999) 6146) predicted a shift of 0.72 eV due to filling of the d-band by electrons from the Re substrate. This d-band filling, in turn, has the expected effect on oxygen reduction kinetics, lowering chemisorption energy for O₂ and thus the kinetics of the ORR, as shown by the kinetic results in Figure 3b. While the results with the model Pd/Re(0001) system are not of practical interest, the clear correlation to electronic properties of the surface, which can be accurately calculated for nearly any surface one can conjure up, is extremely significant and encouraging.

Conclusions

Proof-of-principle experiments indicate that synthesis of Pt as a "skin" on bimetallic nanoparticles could enable Pt loadings in the PEMFC air cathode to be lowered by as much as a factor of 5 from present (optimized) levels, e.g. from 1 g per kW to 0.2 g per kW. Comparable experiments with Pd thin films indicate an even greater reduction in Pt group metal (PGM) loading is possible for the hydrogen electrode, comparable to the PGM content of the catalytic converter in current typical internal combustion engine vehicles.

Publications

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